EXECUTIVE SUMMARY

Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990

Purpose of this report. Title IV of the 1990 Clean Air Act Amendments (CAAA) set target reductions for sulfur and nitrogen emissions from industrial sources as a means of reducing the acidity in deposition. One of the intended effects of the reductions was to decrease the acidity of low alkalinity waters and thereby improve their biological condition. *The purpose of this report is to assess recent changes in surface water chemistry in the northern and eastern U.S., in response to changes in deposition.* The regions covered in this report are New England (sites in Maine, New Hampshire, Vermont and Massachusetts), the Adirondack Mountains of New York, the Northern Appalachian Plateau (New York, Pennsylvania and West Virginia), the Ridge and Blue Ridge provinces of Virginia, and the Upper Midwest (Wisconsin and Michigan). The data covered in this report are from 1990 through 2000, the period since the last major science review by the National Acidic Precipitation Assessment Program (NAPAP).

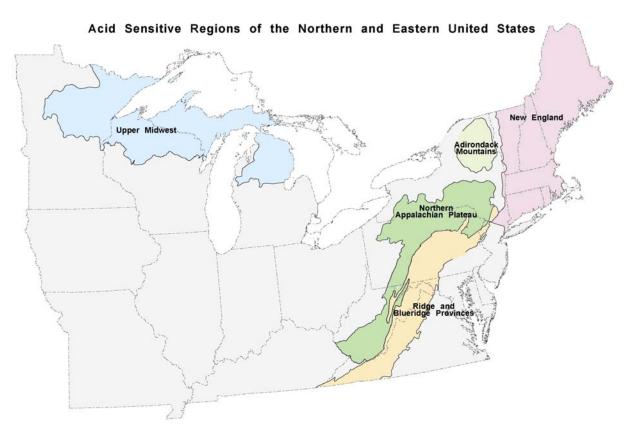


Figure A. Acid sensitive regions of the northern and eastern United States; this report assesses trends in surface waters in each of these regions.

Substantial reductions in emissions of sulfur have occurred in the past 30 years, with the rate of decline accelerated by Phase I of the 1990 CAAA, implemented in 1995. Modest reductions in nitrogen emissions have occurred since 1996. The key questions are (a) whether the declines in emissions translate into reductions in acidic deposition; and (b) whether biologically relevant water chemistry has improved in acid sensitive regions. The measures of expected recovery include decreased acidity, sulfate, and toxic dissolved aluminum concentrations.

Anthropogenic acidity in atmospheric deposition. NO_x and SO_x from the combustion of fossil fuels react with water in the atmosphere to produce acid rain, a dilute solution of nitric and sulfuric acids. This acidity (and the acid anions sulfate and nitrate) may travel hundreds of miles before being deposited on the landscape. The northern and eastern U.S. receives precipitation with mean pH that ranges from 4.3 in Pennsylvania and New York, to 4.8 in Maine and the Upper Midwest. The acidity (hydrogen ion concentration) in precipitation in the eastern U.S. is at least twice as high as in pre-industrial times. Atmospheric deposition is one of the most ubiquitous non-point sources of chemicals to ecosystems.

Acid-base status of surface waters. The 1984-86 EPA National Surface Water Survey (NSWS) estimated the number of acidic waters at 4.2% of lakes and 2.7% of stream segments in acid-sensitive regions of the North and East. Acidic waters are defined as having acid neutralizing capacity (ANC) less than zero (i.e., no acid buffering capacity in the water), corresponding to a pH of about 5.2.

This report addresses the recent chemical responses in the surface waters in five regions of the North and East that are considered sensitive to acidic deposition. The data in this report are largely from the EPA Long Term Monitoring (LTM) and the EPA Temporally Integrated Monitoring of Ecosystems (TIME) projects, part of EMAP (Environmental Monitoring and Assessment Program). The regions include lakes in the Adirondacks, central and northern New England, and the upper Midwest. Sensitive regions with small streams are found in the mid-Atlantic region, including the northern and central Appalachian Plateau and the Ridge and Blue Ridge provinces. Surface waters in most other regions are not sensitive to the impacts of acidification due to the nature of the local geology.

Recent changes in atmospheric deposition. We evaluated the changes in atmospheric deposition from the five regions during 1990-2000, using National Atmospheric Deposition Program (NADP) data. Sulfate declined significantly at a rate between -0.75 and -1.5 μeq/L/year. There was a sharp drop in sulfate concentrations in 1995 and 1996, followed by a modest increase in 1997-2000, in parallel with emissions. Nitrogen (nitrate + ammonium) declined slightly in the Northeast, and increased slightly in the Upper Midwest; most of these changes can be attributed to changes in nitrate deposition. Base cations in deposition, which are important for the neutralization of acidity in precipitation and in watersheds, showed no significant changes during the decade in the East, and increased slightly in the Upper Midwest. These changes in deposition are a continuation of trends that pre-date the 1995 implementation of Phase I of the CAAA, and are consistent with other recent published analyses of changes in regional deposition patterns.

Recent changes in acid base status in surface waters. All regions except the Ridge/Blue Ridge province in the mid-Atlantic showed significant declines in sulfate concentrations in surface

waters, with rates ranging from -1.5 to -3 μ eq/L/year (Figure B). These declines were consistent with the decline in sulfate in precipitation. Nitrate concentrations decreased in two regions with the highest ambient nitrate concentration (Adirondacks, Northern Appalachian Plateau) but were relatively unchanged in regions with low concentrations. Dissolved Organic Carbon (DOC) increased in each region, potentially contributing natural organic acidity to offset the recovery from decreased acidity and sulfate in deposition.

Acid neutralizing capacity is a key indicator of recovery, as it reflects the capacity of watersheds to buffer inputs of acidity. We expect increasing values of either ANC or pH (or both) in response to decreasing deposition of sulfur and nitrogen from the atmosphere. ANC increased in three of the regions (Adirondacks, Northern Appalachian Plateau and Upper Midwest) at a rate of $+1~\mu eq/L/year$, despite a decline in base cations (calcium + magnesium) in each region (Figure B). The decline in base cations offsets some of the decline in sulfate, and thus limits the increase in ANC or pH. In the Adirondacks and Northern Appalachians, surface water ANC and pH both increased significantly in the 1990s; toxic aluminum concentrations also declined slightly in the Adirondacks. Regional surface water ANC did not change significantly in New England or in the Ridge/Blue Ridge.

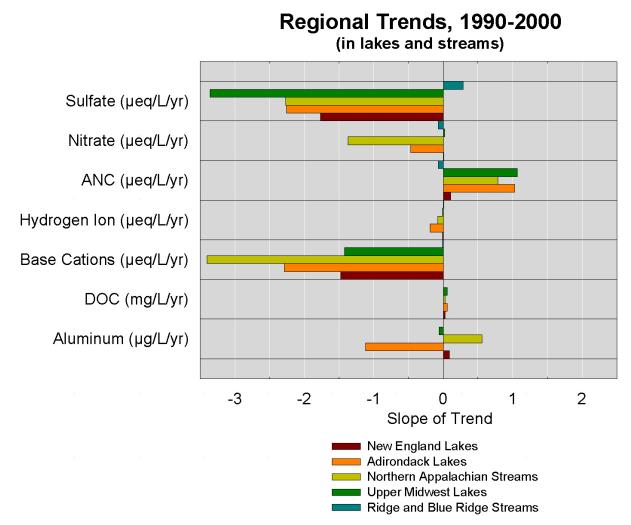


Figure B. Summary of regional trends in surface water chemistry in regions covered by this report.

Has the number of acidic waters changed? Modest increases in ANC have reduced the number of acidic lakes and stream segments in some regions. We estimate that there are currently 150 Adirondack lakes with ANC less than 0, or 8.1% of the population, compared to 13% (240 lakes) in the early 1990s. In the Upper Midwest, an estimated 80 of 250 lakes that were acidic in mid-1980s are no longer acidic. TIME surveys of streams in the northern Appalachian Plateau region estimated that 5,014 kilometers of streams (ca. 12%) were acidic in 1993-94. We estimate that 3,600 kilometers of streams, or 8.5%, remain acidic in this region at the present time. In these three regions, approximately one-quarter to one-third of formerly acidic surface waters are no longer acidic, although still with very low ANC. We find little evidence of a regional change in the acidity status of New England or the Ridge/Blue Ridge regions and infer that the numbers of acidic waters remain relatively unchanged. There is no evidence that the number of acidic waters have increased in any region, despite a general decline in base cations and a possible increase in natural organic acidity.

Do changes in deposition translate into changes in surface waters? A major goal of this assessment is to evaluate the effectiveness of emission reductions in changing surface water chemistry. We only make this assessment for sulfate because changes in the deposition of nitrogen have been minor. In New England, the Adirondacks and the Northern Appalachians, the percent declines in sulfate concentrations in precipitation were generally steeper than in surface waters. This is largely as expected and suggests that for a majority of aquatic systems, sulfate recovery exhibits a somewhat lagged response. However, the lakes and streams with the steepest declines in sulfate had very similar rates to those in deposition, indicating that the most responsive watersheds responded directly and rapidly to the sulfate decrease in deposition. As expected, there was little correspondence between rates of sulfate decline in streams and deposition in the Ridge and Blue Ridge provinces due to the adsorptive capacity of the soils in the region. In the upper Midwest, the rate of decline in lakes was greater than the decline in deposition, probably reflecting the residual effects of the drought of the late 1980s. Longer term, we expect the chemistry of seepage lakes in the Upper Midwest to mirror the decline in deposition, similar to the pattern seen in seepage lakes in New England that did not experience the 1980s drought.

Complications for assessing recovery. Declines in atmospheric deposition of sulfate have led to nearly universal declines in sulfate concentrations in surface waters. This response is one simple measure of the intended recovery in surface waters and marks a success of the CAAA and efforts by industry in reducing SO₂ emissions. However, the anticipated decrease in acidity corresponding to the decline in sulfate has been modest.

It is important to recognize that *recovery will not be a linear process*. Moreover, the changes in surface water chemistry reported here have occurred over very short periods relative to the implementation of the CAAA emission reductions in 1995. The decline in sulfate is without question due to the decline in emissions and deposition, but mechanisms producing other changes are much less clear. Other responses in surface waters may be partially attributable to factors other than atmospheric deposition, such as climate change and forest maturation. In particular, some of the observed increase in ANC may result from decreases in nitrate concentrations (e.g., in the Adirondacks and Northern Appalachian Plateau); changes in nitrate are unrelated to changes in nitrogen deposition and are not expected to continue. If the trend toward lower nitrate in surface water reverses, some of the gains in ANC may be lost.

We can identify at least five factors that are important in determining the recovery, or lack of recovery, in surface waters of the northern and eastern U.S. Continued long-term research and monitoring will be necessary to understand the causes, effects, and trends in these processes.

- 1) <u>Base cations</u>. We report declining surface water concentrations of base cations (e.g., calcium, magnesium) in all of the glaciated regions in this report (the Ridge and Blue Ridge region is the only non-glaciated region). At some individual sites, further acidification has occurred because base cations are declining more steeply than sulfate. While decreases in base cation loss from watersheds probably indicates slower rates of soil acidification, they nonetheless limit the magnitude of surface water recovery. Continued long-term research at acid-sensitive sites is needed to determine the cause and effect of the relationship between base cations and sulfate and the effects of cation loss on soil and surface water recovery.
- 2) Nitrogen. Continued atmospheric loading of nitrogen may be influencing the acid-base status of watersheds in yet undetermined ways. Unlike sulfate, concentrations of nitrogen in deposition have not changed substantially in 20 years. Also unlike sulfate, most nitrogen deposited from the atmosphere is retained in watershed soils and vegetation; nitrogen sequestration is not expected to continue ad infinitum (Stoddard 1994, Aber et al., in press). We report that surface water nitrate concentrations are largely unchanged, except in two regions characterized by high nitrate concentrations a decade ago (Adirondacks, Northern Appalachian Plateau). The mechanisms behind these decreases in nitrate are not understood and could include climate change, forest recovery from disturbance, and the effects of land-use history. Future increases in nitrate concentrations in all regions are not improbable and would retard recovery if other factors remain constant.
- 3) <u>Natural organic acidity</u>. Increases in dissolved organic carbon in acid-sensitive waters may have contributed additional natural organic acidity to surface waters, complicating our interpretation of the response in acidity. This factor is an important long-term research question that is probably linked to complex issues including climate change and forest maturation.
- 4) <u>Climate</u>. Climatic fluctuations induce variability in surface water chemistry and thus obscure changes that we expect to result from declining acidic deposition. Climate or climate-related processes may counteract recovery by producing declines in base cations to offset a decline in sulfate or by inducing an increase in natural organic acidity. These interactions of factors underscore the need to continue monitoring a subset of sensitive systems so as to understand the full suite of drivers and responses in ecosystems.
- 5) <u>Lag in response</u>. Documentation of the response of watersheds to changes in atmospheric deposition may take longer than the timeframe of available data. Recovery itself may have an inherent lag time beyond the time scale of currently available monitoring data. Moreover, the changes observed are not unidirectional. Uncertainty with respect to timeframes can only be resolved with continued long-term data.

Indicators of recovery. A main goal of the Title IV of the CAAA is to decrease the acidity of affected surface waters. Although decreases in acidity have occurred in several regions, additional factors appear to point toward recovery, *forecasting* an improvement in biologically

relevant surface water chemistry. It is not yet clear if further reductions in emissions and deposition will be necessary for widespread recovery to occur. These factors forecast the onset of recovery:

- a) Sulfate is an increasingly smaller percentage of total ion concentration in surface waters.
- b) ANC has increased modestly in three of the five regions.
- c) Dissolved Organic Carbon has increased regionally, perhaps toward a more natural preindustrial concentration as acidity decreases in surface waters.
- d) Toxic aluminum concentrations appear to have decreased slightly in some sensitive systems.

Expectations for recovery. An important consideration for measuring the success of the CAAA is to have appropriate expectations for the *magnitude* of potential recovery. Lakes inferred to have been measurably acidified by atmospheric deposition were already marginally acidic, typically with pH less than 6, before anthropogenic atmospheric pollution began more than 100 years ago. Therefore, full recovery of acidic lakes will not yield neutral pH. However, there is evidence that DOC will increase during recovery, and both increasing DOC and increasing pH values will lower the toxicity of aluminum. This change may allow recovery of fish populations to historical conditions even if pH remains low.

Recommendations. In the North and East, there is evidence of recovery from the effects of acidic deposition. The complexities of ecosystem response – effects of forest health, soil status, natural organic acidity, the relative importance of sulfur vs. nitrogen deposition, future emission/deposition scenarios – make predictions of the magnitude and timing of further recovery uncertain. The results of this trend analysis suggest two recommendations for environmental monitoring:

- 1) <u>Deposition monitoring</u>: The analyses in this report depended heavily on the long-term NADP/NTN program for monitoring the chemistry of precipitation. The future assessment of deposition and aquatic trends will depend heavily on these data, and therefore our recommendation is to maintain a national precipitation chemistry network.
- 2) Surface water monitoring: The effectiveness of current or future amendments to the Clean Air Act can best be determined by monitoring the response of subpopulations of sensitive surface waters through time. Long-term records provide the benchmark for understanding trends in ecological responses. The reviewers of early drafts of this report strongly urged the authors to recommend the continuation of the long-term research programs upon which this report is based and the addition of biological monitoring to begin documenting potential biotic recovery.

Future research. The data from these long-term sites will be invaluable for the evaluation of the response of forested watersheds and surface waters to a host of research and regulatory issues related to acidic deposition, including soil and surface water recovery, controls on nitrogen retention, mechanisms of base cation depletion, forest health, sinks for sulfur in watersheds, changes in DOC and speciation of aluminum, and various factors related to climate change. As one reviewer of this report noted, "...these sites have irreplaceable long-term data that should constitute a 'research infrastructure' akin to an EPA laboratory. These sites will help address many basic science issues in which EPA ORD has a continuing interest...." Moreover, as

several of the reviewers observed, long-term data serve as the foundation for ecological research and modeling. Without such data, our ability to ask the right questions is reduced, and our ability to base the answers to these questions on actual data is likewise compromised.